Carbon dioxide activation by a uranium(III) complex derived from a chelating bis(aryloxide) ligand

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Carbon Dioxide Activation by a Uranium(III) Complex Derived from a Chelating Bis(aryloxide) Ligand

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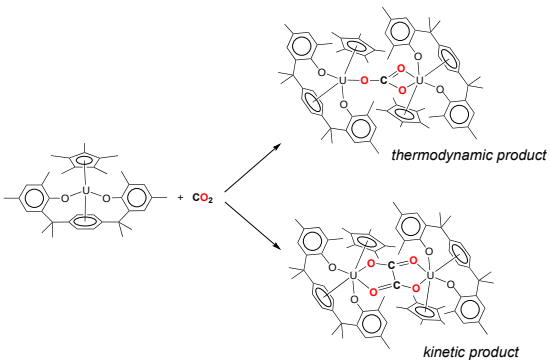
Supporting Information Placeholder



ABSTRACT: The new dianionic ligand, $C_6H_4\{p\text{-}C(CH_3)_2C_6H_2Me_2O^-\}_2$ (= *p*-Me_2bp), featuring two aryloxide donors and a central arene ring, has been synthesized, and used to prepare the mixed-ligand U(III) compound, [U(Cp*)(*p*-Me_2bp)] which exhibits an η^6-interaction with the uranium center. Reductive activation of CO_2 was investigated using [U(Cp*)(*p*-Me_2bp)] in supercritical CO_2, which gave a dinuclear uranium carbonate complex, $\{U(Cp^*)(p\text{-}Me_2bp)\}_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CO_3)$, cleanly and selectively. Reactivity studies in conventional solvents using lower pressures of CO_2 showed the formation of a rare U(IV) oxalate complex, $\{U(Cp^*)(p\text{-}Me_2bp)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2O_2)$, alongside $\{U(Cp^*)(p\text{-}Me_2bp)\}_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CO_3)$. The relative ratio of the latter two products is temperature dependent: at low temperatures (-78 °C) oxalate formation is favored, whilst at room temperature the carbonate is the dominant product. The U(IV) iodide, [U(Cp*)(*p*-Me_2bp)I], was also synthesized and used as part of an electrochemical study, the results of which showed that [U(Cp*)(*p*-Me_2bp)] has a U^{IV}/U^{III} redox couple of −2.18 V vs $FeCp_2^{+/0}$ as well as an possible electrochemically accessible U^{III}/U^{II} reduction process at −2.56 V vs $FeCp_2^{+/0}$.

INTRODUCTION

Since the development of easily accessible U(III) starting materials, the field of uranium(III) chemistry has flourished, utilizing a wide range of ligands to stabilize uranium in this oxidation state-of particular current interest in the context of small molecule activation.[1] Aryloxide groups provide a hard oxygen donor atom, well suited to binding oxophilic uranium in the +3 and higher oxidation states,[2,3] and homoleptic U(III) derivatives of bulky aryloxide ligands have been shown to reductively activate N_2 and CO, and insert CO_2.[4] Meyer *et. al.* pioneered the use of the tripodal ligands derived from phenols of the type ($(^{R,R'}ArOH)_3mes$) which incorporates three aryloxide arms and a central arene ring which provides additional electronic stabilization via a δ interaction with the uranium center.[5] This approach has led to the successful synthesis of a U(II) complex,[6] and the uranium(III) complex [($(^{Ad,Me}ArO)_3mes$)U] which electrocatalytically generates dihydrogen from water.[7] Arnold *et al.* have also reported a tetraaryloxide variant which facilitates the complexation of two uranium centers.[8]

Uranium(III) complexes featuring a variety of ancillary ligand sets have been shown to disproportionate CO_2 to form CO_3^{2-} complexes and CO.[9] Furthermore, we and others have also reported the reductive coupling of CO_2 to yield bridging oxalate U(IV) complexes, which is a rare transformation in uranium chemistry (and indeed in the d-block elements).[10,11] Our work to date on small molecule activation chemistry has focused on the use of a "soft" ligand set around U(III), in the form of a mixed sandwich framework incorporating a cyclopentadienyl ligand and a dianionic aromatic

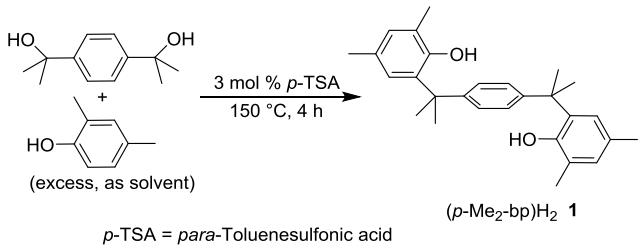
cycloooctatetraene or pentalene ligand.[10,12] Hence we were interested in the effect of changing the dianionic ligand in the latter for an alternative, "harder" chelating ligand with tunable steric demands. Here we report a new bidentate ligand featuring two dimethyl functionalized aryloxide rings and a central arene ring, and the synthesis of its Cp*U(III) derivative and reactivity towards CO_2 thereof. Beyond simply providing steric bulk, the arene is centrally situated to promote stabilization of low valent U centers *via* δ-backbonding (*vide supra*).

RESULTS AND DISCUSSION

Ligand synthesis

The neutral bisphenol (*p*-Me_2bp)H_2 (**1**) was prepared *via* a modification of a procedure reported in the patent literature.[13] α,α,α',α'-Tetramethyl-1,4-benzenedimethanol undergoes an acid catalyzed condensation reaction with 2,4-dimethylphenol (excess, as solvent) to give crude **1** (Scheme 1). Recrystallization from Et_2O gave **1** as white crystals in 40-50% overall yield, with analytical purity confirmed by elemental analysis.

Scheme 1. Synthesis of (*p*-Me_2bp)H_2 (1)



The solid state molecular structure of **1** was determined by X-ray diffraction, and is shown in Figure 1, together with selected bond lengths and angles. The phenol rings adopt an *anti* conformation with respect to the central arene, and the quaternary sp^3 carbon (C9) linking the phenol and arene rings is tetrahedral (C6–C9–C12 angle of 109.05(10)°) consistent with a lack of strain. The central arene C–C distances are essentially the same as those observed in the solid state structure of *p*-xylene (**1**: av. 1.3930 Å; *p*-xylene: av. 1.392 Å) and the central arene displays almost no ring torsion (**1**: +/- 0.15°, *p*-xylene: +/- 0.10°).[14] The two phenol rings are related *via* a crystallograpic inversion center and the angle between the planes of the central arene and each phenol ring is 81.51°.

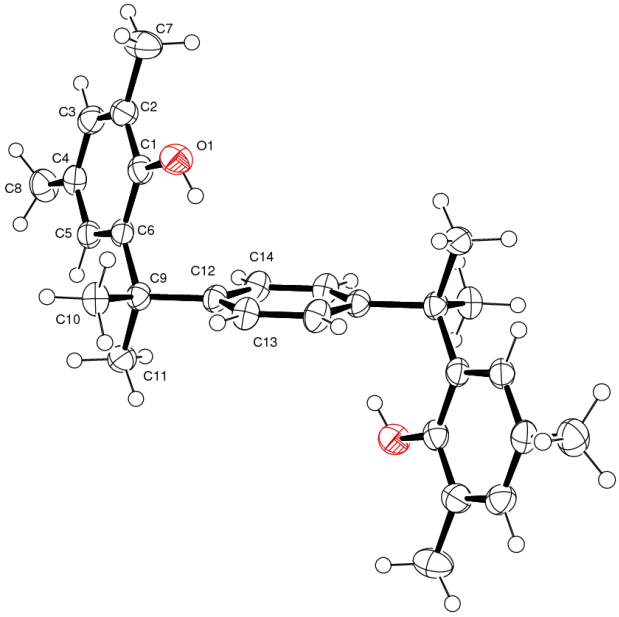


Figure 1. ORTEP diagram for molecular structure of compound **1**. Disordered C_6D_6 solvent omitted for clarity; thermal ellipsoids at 50%. The numbering scheme is used for NMR spectroscopy assignments. Selected structural parameters (Å, deg): C12–C13 = 1.390(17), C12–C14 = 1.3933(18), C6–C9–C12 = 109.05(10), C1–O1 = 1.3843(15).

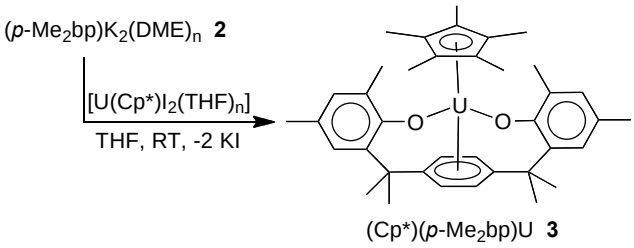
^{1}H and ^{13}C NMR spectroscopic data show two-fold symmetry, indicating that in solution the phenol rings freely rotate around the $C(CH_3)_2$ units linking them and the central arene ring.

Bisphenol **1** is readily deprotonated by 2 equivalents of KH in 1,2-dimethoxyethane (DME) to give the dipotassium salt (*p*-Me_2bp)K_2(DME)$_n$ (**2**) as a fractional solvate (n = 1.5 - 2) in 85-95% yield. The crude material thus obtained returned elemental analyses which were slightly high in C and H, however it was successfully used in subsequent salt metathesis reactions without further purification. Compound **2** is sufficiently soluble in d_5-pyridine to allow the degree of DME solvation in individual samples to be determined by ^{1}H NMR spectroscopy, however, these solutions were too dilute to allow acquistion of ^{13}C NMR spectroscopic data.

Mixed Ligand uranium(III) complex

Dipotassium salt **2** reacts with 1 equivalent of [UCp*I_2(THF)$_n$] (prepared *in situ* in THF) to give, after workup, the mononuclear U(III) complex [U(Cp*)(*p*-Me_2bp)] (**3**) as dark green-black plates in yields of 60 - 75% (Scheme 2).

Scheme 2. Synthesis of [U(Cp*)(*p*-Me$_2$bp)] (3)



Complex **3** is soluble in hydrocarbons and ethers, and single crystals suitable for X-ray crystallography were obtained by recrystallisation from pentane at −50 °C. The asymmetric unit contains two crystallographically independent molecules of **3** (Figure 2) featuring the bisaryloxide ligand in a *syn* conformation, allowing both aryloxide oxygens to chelate to the U center with an average U–O distance of 2.179 Å, which is within the range observed for other U(III) aryloxides (2.155 - 2.338 Å).[15] The Cp* ring assumes the usual η^5-binding mode (av. Ct(Cp*)–U = 2.487 Å) whilst the central arene ring is planar (max. deviation from C_6 plane 0.038 Å) and bound to the U center *via* an η^6-arene interaction with an average U–C(arene) distance of 2.774 Å. This is similar to the U–C(arene) distance in the mesityl-anchored chelating U(III) complex $C_6Me_3\{CH_2C_6H_2{}^tBu_2O\}_3U$ (av. 2.73 Å),[5] and somewhat shorter than other U(III) complexes featuring pendant arenes (e.g. $(2,6\text{-}Ph_2\text{-}4\text{-}Me\text{-}C_6H_3\text{-}O)_3U$, 2.853 Å; $(2,6\text{-}Ph_2\text{-}4\text{-}Me\text{-}C_6H_3\text{-}O)_3U(THF)$, 2.964 Å)[16] and discrete arenes (e.g. $(C_6Me_6)U(AlCl_4)_3$, 2.93 Å;[17] $(C_6Me_6)U(BH_4)_3$, 2.93 Å).[18] The central arene C–C distances in **3** (av. 1.411 Å) are slightly longer than observed in **1** (av. 1.393 Å). Interestingly, the metal center bears no coordinated Lewis base (*i.e.* THF), unlike, for example, the mixed sandwich complexes $[U(\eta^8\text{-}C_8H_6\{SiMe_3\text{-}1,4\}_2)(\eta^5\text{-}C_5Me_4R)(THF)]$ (R= Me, Et, ^{i}Pr, ^{t}Bu).[10]

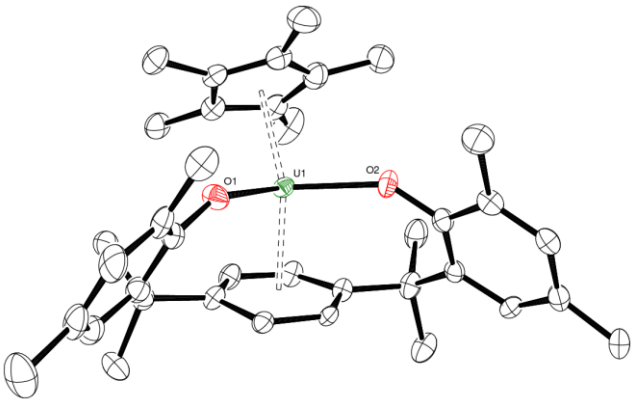


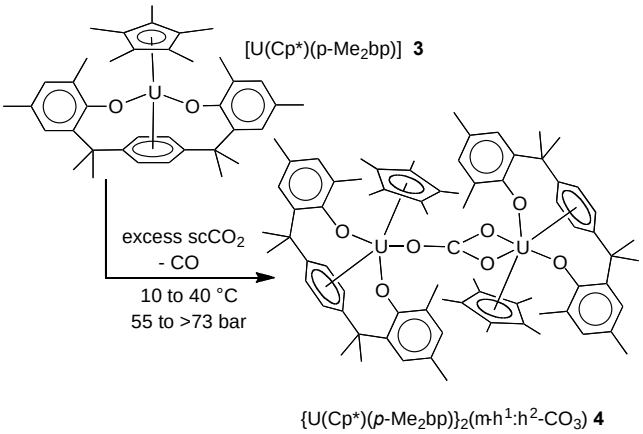
Figure 2. ORTEP diagram for molecular structure of compound **3**. One crystallographically independent molecule shown with 50 % thermal ellipsoids, H atoms omitted for clarity. Selected structural parameters (Å, deg): average U–O = 2.179, average U–C(arene) = 2.774, average Ct(arene)–U = 2.388 average Ct(Cp*)–U = 2.487, average O1–U–O2 = 117.9.

The ^{1}H NMR spectrum of paramagnetic **3** contains resonances over the range 18.3 to −13.5 ppm. Both the CH_3 groups of the bridging arms and the central arene protons appear as two distinct sets of resonances due to the reduced symmetry imposed by a rigid aryloxide and Cp* coordination environment.

Carbon dioxide activation

The reaction of gases with f-element complexes in the solid state (i.e. solvent-free) has recently been reported as a potentially high yielding and selective approach to exploring subsequent reduction chemistry.[19] Recent work from our own laboratory has used supercritical CO_2 to promote the exclusive formation of U(IV) bridging carbonate complexes,[10] and this approach was used to investigate the reductive activation of CO_2 by **3** (Scheme 3).

Scheme 3. Synthesis of {U(Cp*)(*p*-Me$_2$bp)}$_2$(μ-η^1:η^2-CO$_3$) (4)



The reaction of solid **3** in supercritical CO_2 resulted in an immediate color change from green-black to orange, and the resultant orange powder contained only one major product (>96% by ^{1}H NMR spectroscopy), confirming the highly selective nature of the reaction. The product was identified as the bridging carbonate complex $\{U(Cp^*)(p\text{-}Me_2bp)\}_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CO_3)$ (**4**) by X-ray diffraction studies crystals of **4.C$_6$H$_6$** obtained from C_6H_6 at ambient temperature. The degree of solvation in **4.C$_6$H$_6$** was determined by ^{1}H NMR spectroscopy in d_8-THF, and satisfactory elemental analysis obtained for this solvate.

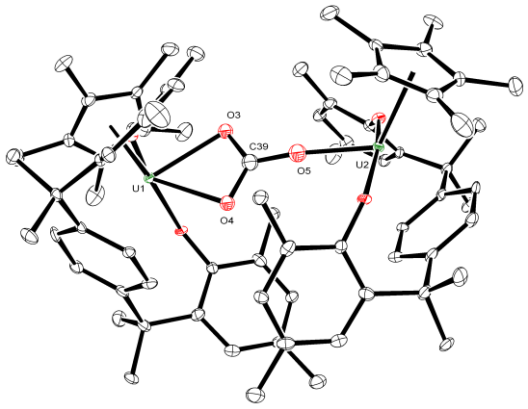


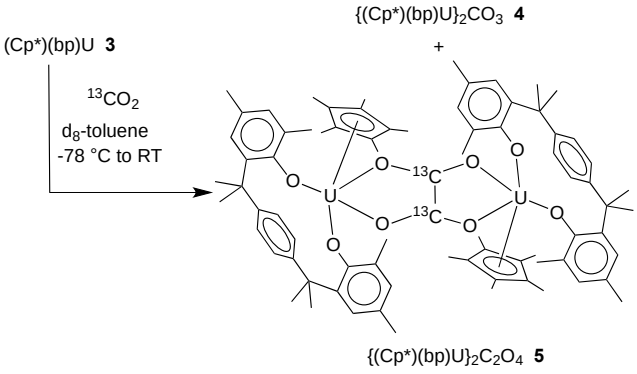
Figure 3. ORTEP diagram for molecular structure of compound **4**; 50 % thermal ellipsoids shown. Solvent masking was employed to remove a highly disordered C_6H_6 from the refinement. Selected structural parameters (Å, deg): average U─O(aryloxide) = 2.175, η^1-U2─O5 2.162(11), average η^2-U─O = 2.448, average U─C(arene) = 3.124, Ct(arene) ─U = 2.7902(3), Ct(Cp*)─U = 2.4958(3), O1─U1─O2 = 161.6(3).

The solid state molecular structure of **4** is shown in Figure 3, together with selected bond distances and angles, and reveals a dinuclear structure with a η^1:η^2-bound carbonate bridging two uranium centers. The central CO_3^{2-} unit is disordered in the crystal, resulting in superposition of η^1:η^2 and η^2:η^1 binding modes with 50:50 occupancy. The resulting model required isotropic refinement for the central carbonate (which has a regular planar triangular structure), and as a result the bond lengths and angles within the central carbonate unit cannot be determined accurately. The η^1-U─O distance (2.162(11) Å) is shorter than the η^2-U─O distances (av. 2.448(15) Å), a feature which was also observed in the mixed sandwich U(IV) carbonate complex $\{U(\eta^8\text{-}C_8H_6\{Si^iPr_3\text{-}1,4\}_2)(\eta^5\text{-}C_5Me_4H)\}_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CO_3)$ (η^1: 2.227(12) Å, η^2: av. 2.422(10) Å).[9b] Each U center is chelated by a pair of bisaryloxide oxygens (av. U─O = 2.175 Å), with the central U─arene interaction (av. U─C(arene) = 3.124 Å) significantly weaker than observed in **3**, possibly due to the larger number of O donors and greater steric congestion in **4**. This weak U─arene interaction is consistent with a pair of U(IV) centers each binding to a neutral, unreduced central arene. The complex is twisted around the central carbonate unit to minimise steric interaction between opposite bisaryloxides (torsion as measured between opposite arene centroids Ct_1(Arene) ─U_1─U_2─Ct_2(Arene) = 67.95 °).

The torsion observed in the solid state structure of **4.C$_6$H$_6$** persists in solution. At 0 °C the ^{1}H NMR spectrum of **4** ($C_6D_5CD_3$) consists of eight CH resonances, eight CH_3 resonances and one resonance for the two freely rotating Cp* ligands paramagnetically shifted between 33.0 and −67.1 ppm. Above 10 °C the aryloxide resonances exhibited varying degrees of coalescence in addition to the changes in chemical shift expected for a paramagnet, but there was no resolution to a discrete, higher symmetry species even at 100 °C.

The reductive activation of $^{13}CO_2$ by **3** was also investigated in solution (Scheme 4). An excess (*ca.* 2 equivalents) of $^{13}CO_2$ was added to a solution of **3** in $C_6D_5CD_3$ at −78 °C using a Töpler pump. Upon warming to ambient temperature the colour changed from black to orange, and the ^{1}H NMR spectrum showed the presence of a mixture of products, including **4** (*ca.* 40%). In addition to excess $^{13}CO_2$ and free ^{13}CO (arising from the reductive disproportionation of $^{13}CO_2$ to form **4**), three paramagnetically shifted resonances were observed in the $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture. A singlet at −101 ppm, which was assigned to the bridging $^{13}CO_3$ in **4**, and two mutually coupled doublets at −130 and −199 ppm; all three resonances remained unchanged in the ^{1}H coupled spectrum. The observed coupling in the latter is consistent with coupling between two proximal, inequivalent ^{13}C atoms (J_{CC} = 70 Hz), thus pointing towards the formation of an oxalate complex resulting from the reductive coupling of $^{13}CO_2$.

Scheme 4. Synthesis of $\{U(Cp^*)(p\text{-}Me_2bp)\}_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CO_3)$ (4) and $\{U(Cp^*)(p\text{-}Me_2bp)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2O_2)$ (5)



Fractional crystallization from benzene and then diethyl ether produced yellow crystals of the bridging oxalate complex **5** suitable for single crystal X-ray diffraction. The molecular structure is shown in Figure 3, together with selected bond lengths and angles, and shows a η^2:η^2 bridging oxalate unit in which the two carbons are inequivalent (the two Cp* ligands are effectively cis to one another), and hence consistent with ^{13}C NMR data. Of note is the O1─C1─C2─O2 torsion angle of 22.2(12)° which is not seen in the molecular structures of $\{U(\eta^8\text{-}C_8H_6\{SiMe_3\text{-}1,4\}_2)(\eta^5\text{-}C_5Me_4{}^iPr)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2O_4)$,[10] or $\{((^{nP,Me}ArO)_3tacn)U^{IV}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2O_4)$[11] possibly due to the steric hindrance around the uranium center. The U─O(oxalate), and oxalate C─C and C─O bonds are, however, consistent with those found in the latter U(IV) oxalate complexes. The arene centroid to uranium distance of 3.151 Å indicates that there is no interaction between the uranium center and the central arene ring in **5**.

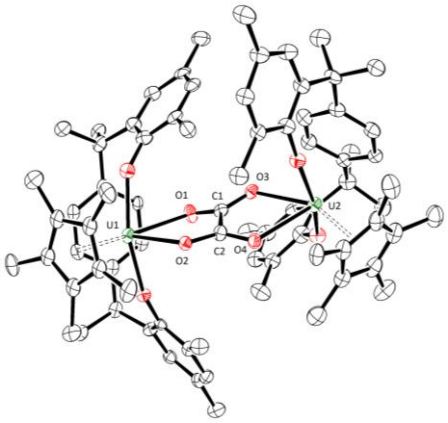


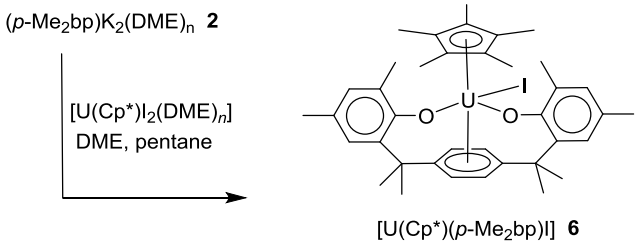
Figure 3. ORTEP diagram for molecular structure of compound **5**; 50 % thermal ellipsoids shown. Selected structural parameters (Å, deg): C1─C2 = 1.531(12), O1─C1─C2─O2 torsion angle = -22.2(12), average U─O(aryloxide) = 2.147, average Ct(Cp*)─U = 2.5030, Ct(arene)─U = 3.151(8), average O─U─O (aryloxide) = 160.6, Ct(Cp*)─U─Ct(arene) = 120.184(14).

To gain further insight into the distribution of products **4** and **5** formed from **3** and $^{13}CO_2$, the reaction was repeated but the reaction mixture was allowed to react at −78 °C for two days followed by slow warming to room temperature over one day. This furnished a mixture of **4**:**5** in a ratio of 30:70 as judged by the relative integration of the Cp* resonances in the ^{1}H NMR spectrum of the crude reaction mixture. When addition of $^{13}CO_2$ to **3** at −78 °C was followed by rapid equilibration to room temperature the ratio of **4**:**5** was found to be 83:17 suggesting that **5** is the kinetic product while **4** is the thermodynamic product. The above observations suggest that the formation of **4** competes with the formation of **5** and the two pathways can be kinetically manipulated.

Uranium(IV) iodide complex

An attempt to prepare **3** using DME as solvent instead of THF using an equimolar amount of **2** and [UCp*I_2(DME)$_n$] produced *in-situ* from UI_3 and KCp* in DME, resulted in white solids (presumed to be KI) and a dark brown solution which contained several new products, but no **3** by ^{1}H NMR spectroscopy (Scheme 5). The uranium (IV) iodo complex **6** was isolated from this solution as a microcrystalline red powder in 29% yield, and its formation from a U(III) starting material must presumably involve a disproportionation reaction, thus explaining the modest yield of **6**. Single crystals of **6** suitable for X-ray diffraction were obtained from THF and furnished **6.THF** which was used for NMR and MS studies. Satisfactory elemental analysis results were obtained for **6.THF**.

Scheme 5. Synthesis of [U(Cp*)(*p*-Me$_2$bp)I] (6)



The molecular structure of **6** displays a *syn*-aryloxide chelating to a U center which is η^6-bound to the central arene weakly (av. U─C(arene) = 2.985 Å), consistent with a U(IV) center (Figure 4). The U─O distances (av. 2.149 Å) are similar to those observed in the U(IV) complex **4** and the U─I bond length of 3.0573(6) Å is typical for a U(IV) iodide, *e.g.* 3.059(2) Å in Cp_3UI.[20] Complex **6.THF** is soluble in ethers and aromatic solvents, and the ^{1}H NMR spectrum (C_6D_6) of **6.THF** shows eleven peaks paramagnetically shifted over the range 37.2 to −64.9 ppm. Two sets of *meso*-CH_3 and central arene proton resonances indicate a nonfluctional bisaryloxide coordination environment, as observed for **3**.

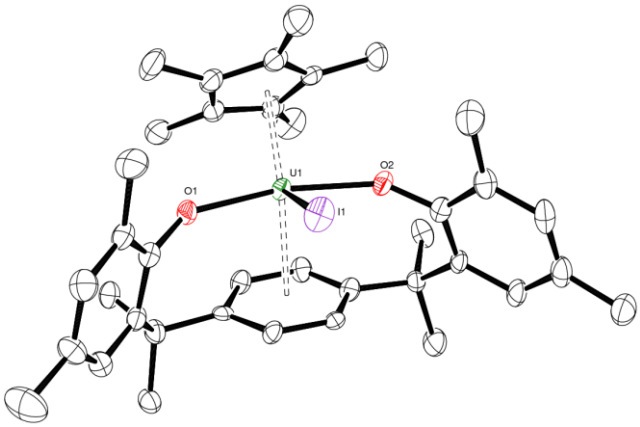


Figure 4. ORTEP diagram for molecular structure of solvent-free **6**; 50 % thermal ellipsoids shown, H atoms removed for clarity. Selected structural parameters (Å, deg): average U─O = 2.149, U─I = 3.0573(6), average U─C(arene) = 2.985, Ct(arene)─U = 2.6381(3), Ct(Cp*)─U = 2.4788(3), O1─U─O2 = 159.18(16), Ct(Cp*)─U─Ct(arene) = 130.181(8).

Electrochemistry

To investigate the redox behavior of the bis(aryloxide)/Cp* complexes and enable comparison with similar U(III) and U(IV) systems, voltammetric data for **3**, **4,** **5** and **6** were obtained in [^{n}Bu$_4$N][B(C$_6$F$_5$)$_4$]/THF. Tabulated

electrochemical data can be found in the Supporting Information.

The cyclic voltammogram of **3** is quite complex and displays several processes as shown in Figure 5. Four quasi-reversible processes were observed at −2.56, −2.18, −1.71 and +0.13 V vs $FeCp_2^{+/0}$. In addition, the CV of **3** shows a minor oxidation feature at *ca*. −1 V vs $FeCp_2^{+/0}$.

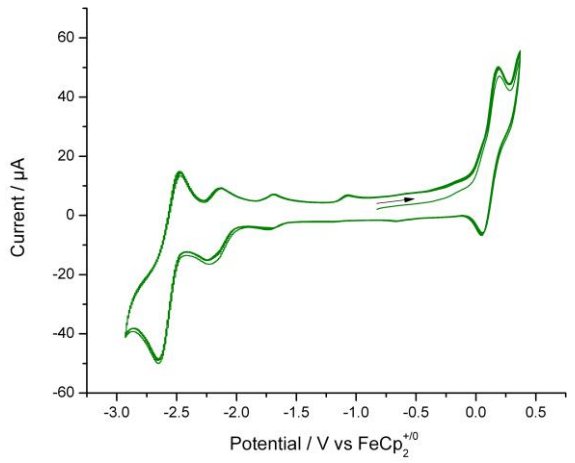


Figure 5. Overlaid CV scans (10 cycles) for **3** in THF / 0.05 M $[^nBu_4N][B(C_6F_5)_4]$, scan rate 100 mV s^{-1}.

Cyclic voltammetry was carried out on the U(IV) derivative **6** to gain insight into the nature of the processes seen in **3**. Complex **6** shows an irreversible reduction wave at −2.19 V vs $FeCp_2^{+/0}$ (Figure S4) which is in excellent agreement with the quasi-reversible process at −2.18 V vs $FeCp_2^{+/0}$ seen in **3** and is assigned to the U^{IV}/U^{III} couple in this system. This value is similar to other U^{IV}/U^{III} redox couples found in other U^{III} systems studied by us and others[10,21] and is consistent with a strongly reducing metal center. Further supporting this assignment is the observation of a single quasi-reversible reduction process at −2.19 V vs $FeCp_2^{+/0}$ in the dinuclear U(IV) complex, **4** (Figure S2).

Upon scanning to more negative potentials **3** and **6** showed a quasi-reversible process observed at −2.56 and −2.59 V vs $FeCp_2^{+/0}$ respectively. This process lies at an extremely negative potential and may be attributable to a ligand based reduction, however, the free ligand **2** did not show a cathodic process within this potential region (Figure S1). Another possibility is a U^{III}/U^{II} reduction process, and Meyer and co-workers have recently reported a trivalent uranium monoarene complex derived from the chelating tris(aryloxide)arene ligand, $[\{(^{Ad.Me}ArO)_3\text{-mes}\}U^{III}]$, which shows a nearly reversible and chemically accessible reduction at −2.495 V vs $FeCp_2^{+/0}$.[22]

When **4** was studied in 0.1 M $[^nBu_4N][PF_6]$ / THF the first U^{IV}- to U^{III} reduction event occurs at −2.25 V vs $FeCp_2^{+/0}$ (Figure S3). For comparison reduction processes in the carbonate-bridged complexes based on the $[U(\eta^8\text{-}C_8H_6\{SiMe_3\text{-}1,4\}_2)(\eta^5\text{-}C_5Me_4R)]$ (R = Et, ^{i}Pr or ^{t}Bu) mixed-sandwich ligand system were observed between −2.11 and −2.17 V vs $FeCp_2^{+/0}$ in 0.1 M $[^nBu_4N][PF_6]$ / THF. [10]

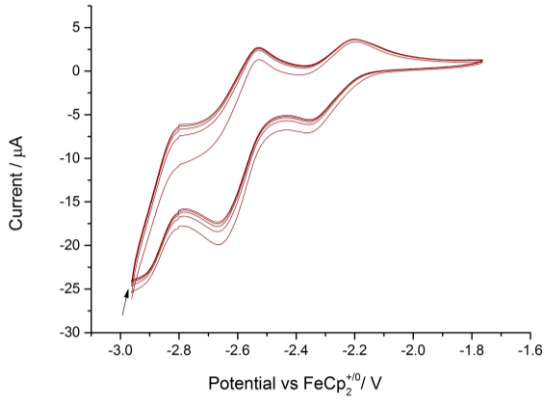


Figure 6. Overlaid CV scans (5 cycles) for **5** in THF / 0.05 M $[^nBu_4N][B(C_6F_5)_4]$, scan rate 100 mV s^{-1}.

The electrochemistry of **5** was studied in 0.05 M $[^nBu_4N][B(C_6F_5)_4]$ / THF and showed two quasi-reversible events at −2.24 and −2.56 V vs $FeCp_2^{+/0}$. These processes are assigned to the $[U^{IV}\text{-}U^{IV}]/[U^{IV}\text{-}U^{III}]^-$ and $[U^{IV}\text{-}U^{III}]^-/[U^{III}\text{-}U^{III}]^{2-}$ couples based on reasonable agreement with corresponding processes observed in **3**, **4**, **6** and in $[U(\eta^8\text{-}C_8H_6\{SiMe_3\text{-}1,4\}_2)(\eta^5\text{-}C_5Me_4{}^iPr)]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2O_4)$.[10] Peak current ratios (i_{pc}/i_{pa}) for these processes of 1.32 and 1.72 respectively indicate that the species generated on the cathodic scan are not completely oxidised back on the return anodic scan. The $\Delta E_{1/2}{}^{(I)-(II)}$ value of 320 mV is indicative of a metal-metal interaction. Two minor anodic processes were observed at −520 and −1007 mV, which we are unable to assign with any certainty.

CONCLUSION

The combination of the soft pentamethylcyclopentadienyl ligand and a hard, chelating aryloxide ligand affords the U(III) complex [U(Cp*)(*p*-Me_2bp)] whose U^{IV}/U^{III} redox couple is essentially identical to that of the mixed sandwich complexes of the type $U(\eta\text{-}C_8H_6\{SiR_3\text{-}1,4\}_2)(\eta\text{-}C_5Me_4R')$. The work presented here demonstrates that the new ligand, $(p\text{-}Me_2bp)^{2-}$, in [U(Cp*)(*p*-Me_2bp)] can significantly alter the reactivity towards CO_2. The new bidentate ligand presented can be synthesized cleanly in moderate yield and provide a system analogous to the COT and pentalene based mixed sandwiches already established in actinide chemistry. Using this ligand a U(III) complex has been used to reductively disproportionate and reductively couple CO_2 to give uranium carbonate and oxalate complexes respectively. Studies have shown reactivity towards CO_2 can be controlled *via* temperature. Electrochemical studies show the U^{IV}/U^{III} couple has a reduction potential of −2.18 V vs $FeCp_2^{+/0}$, indicating this system is an ideal candidate to support metal centers for the activation of small molecules.

Future studies will focus on the reactivity of [U(Cp*)(*p*-Me_2bp)] towards other small molecules, alongside the modification of the $(p\text{-}Me_2bp)^{2-}$ ligand which may lead to the discovery of new reactivity towards substrates.

EXPERIMENTAL SECTION

General Information. All manipulations involving air- or moisture-sensitive materials were performed under an inert atmosphere of argon using standard Schlenk techniques, or in an MBraun N_2 or Ar-filled glovebox. Solvents were dried over appropriate drying agents ($NaK_{2.8}$: pentane, Et_2O, ^{t}BuOMe; K: THF, benzene, toluene) before distilling under N_2 and degassing before use. Solvents were stored over K mirrors with the exception of THF and Et_2O, which were stored over activated 4Å molecular sieves. Deuterated solvents were dried over K, vacuum distilled and freeze-pump-thawed before storage under N_2. NMR spectra were recorded on a Varian VNMR 400 MHz spectrometer at 303 K, with ^{1}H NMR spectra run at 399.5 MHz and ^{13}C NMR spectra run at 100.5 MHz. Chemical shifts are quoted in parts per million and are referenced internally to residual protic solvent shifts (^{1}H) or deuterated solvent shifts (^{13}C). EI-MS was performed by Dr. A. K. Abdul-Sada at the University of Sussex using a VG Autospec Fisions instrument (EI at 70 eV). Elemental analyses were performed by Mikroanalytisches Labor Pascher or Bristol University Microanalytical Laboratory. $^{13}CO_2$ (99.7% enrichment) gas was purchased from EuroIsotop and was transferred *via* an accurately calibrated Töpler pump. The reaction with supercritical CO_2 (99.999% BOC) was performed in a 10 mm sapphire NMR tube equipped with a titanium valve, connected to a high pressure stainless steel line equipped with a high pressure piston pump (High Pressure Equipment Company).

Caution: *Depleted uranium is a weak α-emitter (4.197 MeV) with a half-life of 4.47 x 10^9 years. All manipulations should be undertaken in a well ventilated and monitored fumehood or under an inert atmosphere in a glovebox, and uranium containing residues should be disposed of according to local regulations.*

(*p*-Me$_2$bp)H$_2$ (1). α,α,α',α'-tetramethyl-1,4-benzenedimethanol (10 g, 50 mmol) dissolved in 2,4-dimethylphenol (20 g) was added with stirring over 4 h to 2,4-dimethylphenol (45 g) containing p-tolylsulfonic acid (0.30g, 1.5 mmol, 3 mol %) at 150 °C. Na_2CO_3 (0.60 g, 5 mmol) was added to neutralise the catalyst and the mixture stirred another 40 min. Excess 2,4-dimethylphenol was distilled off under vacuum and the solid, beige coloured reside taken up in Et_2O, rinsed with NaOH (0.6 M, 1 x 100 mL), water (3 x 150 mL), brine (2 x 50 mL), dried over $MgSO_4$ and stripped to provide a crude white solid. Recrystallisation from Et_2O at -50 °C and drying for 2 h (80 °C, 0.01 mbar) provided **1** as a white powder (9.5 g, 23.6 mmol, 47 %). ^{1}H NMR (assigned according to Figure 1) ($CDCl_3$, 303 K) δ 7.36 (s, 4H, H13,14), 7.18 (s, 2H, H5), 6.95 (s, 2H, H3), 4.28 (s, 2H, OH), 2.39 (s, 6H, H8), 2.18 (s, 6H, H7), 1.73 ppm (s, 12H, H10,11). ^{13}C{^{1}H} NMR (assigned as per Figure 1) ($CDCl_3$, 303 K) δ 149.9 (C2), 147.3 (C12), 134.6 (C6), 130.4 (C3), 129.1 (C4), 127.1 (C13,14), 126.2 (C1), 124.9 (C5), 41.7 (C9), 30.0 (C10,11), 21.2 (C8), 16.4 ppm (C7). Anal. Calcd for $C_{28}H_{34}O_2$: C, 83.54; H, 8.51. Found: C, 83.26; H, 8.49. MS (EI)$^+$: *m*/*z* 402 (M^+).

(*p*-Me$_2$bp)K$_2$(DME)$_{1.65}$ (2). A solution of **1** (2.66 g, 6.62 mmol) in DME (40 mL) was added dropwise over 1 h to a stirred suspension of KH (0.533 g, 13.3 mmol) in DME (60 mL). After 18 h the reaction mixture was cooled to -30 °C for 1.5 h, filtered through a frit, and the solids thus obtained dried *in vacuo* for 2.5 h to give the product as a white powder of sufficient purity for further reactions (3.95 g, 95 %). ^{1}H NMR (C_5D_5N, 303 K) δ 7.43 (s, 4H, Ar-H), 7.42 (s, 2H, Ar-H), 7.11 (s, 2H, Ar-H), 3.51 (s, 6.7H, DME CHs, 6.6H, DME CH_2), 3.29 (s, 9.9H, DME CH_3), 2.54 (s, 6H, Ar-CH_3), 2.33 (s, 6H, Ar-CH_3) 1.90 (s, 12H, C(CH_3)$_2$). Anal. Calcd for $C_{34.6}H_{48.5}O_{5.3}K_2$: C, 66.2; H, 7.79. Found: C, 69.2; H, 8.19.

[U(Cp*)(*p*-Me$_2$bp)] (3). A deep blue-green solution of [UCp*I$_2$(THF)$_n$] was prepared by adding THF (70 mL) to KCp* (0.35 g, 2.0 mmol) and UI_3 (1.24 g, 2.0 mmol), with overnight stirring followed by filtration. To this was added (*p*-Me$_2$bp)K$_2$(DME)$_{2.0}$ (1.12 g, 1.7 mmol, 0.85 equivalents) as a suspension in THF (15 mL). The dark brown reaction mixture was stirred overnight before being stripped to dryness, taken up in pentane (60 mL), filtered through Celite and reduced to *ca*. 15 mL. Slow cooling to -50 °C gave **3** as dark olive green platelets which were rinsed with pentane and dried *in vacuo* (0.94 g, 72 %). Analytically pure **3** was obtained by recrystallisation from pentane at -50 °C. ^{1}H NMR ($C_6D_5CD_3$, 303 K) δ 18.28 (s, 2H, Ar-H), 10.05 (s, 2H, Ar-H), 9.05 (s, 2H, Ar-H), 4.54 (s, 6H, CH_3), 4.14 (s, 6H, CH_3), -2.24 (s, 6H, CH_3), -3.89 (s, 15H, Cp*), -13.56 (s, 2H, Ar-H). Anal. Calcd for $C_{38}H_{47}O_2U$: C, 58.98; H, 6.12. Found: C, 58.96; H, 6.35.

{U(Cp*)(*p*-Me$_2$bp)}$_2$CO$_3$ (4). Complex **3** (75 mg, 0.097 mmol) was placed in the sapphire NMR tube which was then pressurized with CO_2 to 55 bar, causing an immediate change in colour from dark olive-green black to orange. The tube was sealed and warmed to 40 °C, causing the CO_2 to form a supercritical phase, observed as a loss of meniscus and visibly increased density throughout the tube. The tube was maintained at this temperature for 20 minutes before cooling (liquid CO_2 state reestablished) and venting of excess gas. Solid, orange **4** was retrieved inside the glove box (71 mg, 0.044 mmol, 91 %). Solvent-free **4** was used for NMR and MS studies. Crystalline samples of **4.C$_6$H$_6$** spontaneously crystallized out from solutions of **4** in C_6H_6 at room termperature and were used for elemental analysis. ^{1}H NMR ($C_6D_5CD_3$, 273 K) δ 32.89 (s, 6 H, CH_3), 29.69 (s, 6H, CH_3), 28.81 (s, 6H, CH_3), 27.22 (s, 2H, CH), 19.01 (s, 2H, CH), 17.57 (s, 2H, CH), 14.81 (s, 6H, CH_3), 13.76 (s, 2H, CH), 10.64 (s, 6H, CH_3), 5.22 (s, 6H, CH_3), 0.15 (s, 6H, CH_3), -3.94 (s, 6H, CH_3), -10.65 (s, 30H, Cp*), -51.26 (s, 2H, CH), -61.22 (s, 2H, CH), -63.30 (s, 2H, CH), -67.11 (s, 2H, CH). Anal. Calcd for $C_{77}H_{94}O_7U_2(C_6H_6)$: C, 59.14; H, 5.98. Found: C, 59.50; H, 5.61. MS (ESI)$^+$: 1608 *m*/*z* (M^+).

{U(Cp*)(*p*-Me$_2$bp)}$_2$C$_2$O$_4$ (5). A 50 ml Young's ampoule with a was charged with **3** (300 mg, 0.386 mmol) and toluene (3 ml). The solution was cooled to -78 °C and degassed and 4 equivalents of CO_2 gas added. A colour change from black to orange was observed shortly after the addition of CO_2. The reaction mixture was left to stir at -78 °C for 2 d and then at room temperature for 1 d. Volatiles were removed *in vacuo*, benzene (5 ml) was added and the suspension heated at almost reflux and left to slow cool to ambient temperature overnight to afford **4.C$_6$H$_6$** as a microcrystalline red solid. The latter was collected by filtration, washed with benzene (3 x 3 ml) and the washings combined with the original filtrate. This solution was then concentrated to *ca.* 3 ml and allowed to stand at room temperature overnight, depositing a further, small amount of the **4.C$_6$H$_6$** which was filtered off. Finally, the filtrate from this, second crystallization was pumped to dryness, dissolved in Et_2O (3 ml) and stored at -35 °C to give small yellow crystals of **5** (32 mg, 10 %). ^{1}H NMR (C_6D_6, 273 K) δ 39.34 (s, 12 H, CH_3), 31.67 (s, 4 H, Ar-H), 25.45 (s, 4 H, Ar-H), 22.68 (s, 12 H, CH_3), 14.82 (s, 12 H, CH_3), -3.77 (s, 12 H, CH_3), -7.62 (s, 30 H, Cp*), -53.91 (s, 4 H, Ar-H), -62.33 (s, 4 H, Ar-H). Anal. Calcd for $C_{78}H_{94}O_8U_2$: C, 57.28; H, 5.79. Found: C, 57.00; H, 6.02.

[U(Cp*)(*p*-Me$_2$bp)I] (6). A deep blue-green solution of [UI$_2$Cp*(DME)$_n$] was prepared by adding DME (70 mL) to KCp* (0.26 g, 1.5 mmol) and UI$_3$ (0.929 g, 1.5 mmol), stirring for 5 d followed by cannula filtration. To this was added (p-Me$_2$bp)K$_2$(DME)$_{1.66}$ (0.60 g, 0.95 mmol, 0.63 equivalents) as a suspension in DME (15 mL). The dark brown reaction mixture was stirred overnight before filtration through Celite, reduction to 20 mL and layering with pentane (20 mL). The mother liquors were stripped, taken up in toluene (10 mL) and pentane (10 mL) and stirred overnight. The brown mixture was filtered *via* cannula, stripped and ^{t}BuOMe (5 mL) added, giving a dark brown solution which spontaneously deposited red crystals over 3 d at room temperature. These crystals were rinsed with pentane at -78 °C and dried in vacuo to give **6** (388 mg, 0.431 mmol, 29 % based on UI$_3$). Recrystallisation of **6** from THF at -50 °C gave **6.THF** as red crystals which were used for NMR, MS and elemental analysis. ^{1}H NMR (C$_6$D$_6$) δ 37.23 (s, 6H, CH$_3$), 36.39 (s, 6H, CH$_3$), 31.32 (s, 2H, Ar-H), 26.38 (s, 2H, Ar-H), 15.25 (s, 6H, CH$_3$), 3.58 (m, 4H, THF), 1.42 (m, 4H, THF), 1.31 (s, 6H, CH$_3$), -5.59 (s, 15H, Cp*), -53.92 (s, 2H, Ar-H), -64.90 (s, 2H, Ar-H). Anal. Calcd for C$_{38}$H$_{47}$IO$_2$U(C$_4$H$_8$O): C, 51.86; H, 5.70. Found: C, 51.85; H, 5.71. MS (EI)$^+$: *m*/*z* 765 (M$^+$ -THF -Cp*).

X-ray Crystallographic Studies. Data sets for **1**, **3**, **4**, **5**, and **6** were collected on an Agilent Gemini Ultra diffractometer with an Enhance source (Mo Kα) or (Cu Kα) equipped with an Eos CCD area detector and an Oxford Cryosystems low temperature device (173 K), operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The program used for control, integration and absorption correction was CrysalisPro.[23] The crystals were mounted on glass fibre or MiTiGen loops with vacuum oil. All solutions and refinements were performed using the OLEX2 package.[24] All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model. In the case of **4** a highly disordered molecule of benzene was found in the asymmetric unit that could not be successfully modeled and as such it was treated using solvent masking. Single crystal XRD data for **5** were collected by the UK National Crystallographic Service (NCS) at the University of Southampton[25] on a Rigaku FR-E+ Ultra High Flux diffractometer (Mo Kα) equipped with VariMax VHF optics and a Saturn 724+ CCD area detector. The data were collected at 100 or 150 K using an Oxford Cryostreams Cobra low temperature device. An empirical absorption correction was carried out using the MULTI-SCAN program. Data collected by the NCS were processed using CrysAlisPro and unit cell data parameters were refined against all data.

ASSOCIATED CONTENT

Supporting Information

Crystal structure and refinement data for **1**, **3**, **4.C$_6$H$_6$**, **5**, and **6**; electrochemical data; solution ^{1}H NMR spectra for **1-6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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